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by

Mikael Jansson

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Doctorial dissertation to be publicly examined in The Svedberg Lecture Hall, Uppsala University, on September 9,1988, at 10.15, for the Degree of Doctor of Philosophy.

ABSTRACT:
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Influences of counterion hydrophobicity on the formation of ionic micelles were studied from a theoretical model. The degree of micellization of counterions was found to be high even for the least hydrophobic counterion examined, i.e. acetate. By calculating self-diffusion coefficients from the evaluated distribution functions of counterions and amphiphiles and comparing them to experimental self-diffusion data, the relevance of the model could be tested. Good agreements were obtained between the measured and the calculated concentration dependence of the ion self-diffusion coefficients.

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Key words: NMR, Self-Diffusion, Micelles, Vesicles, Counterions.

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List of contents:

This thesis is based on the following papers:

I. **Mikael Jansson, Puyong Li and Peter Stilbs.**
" Dynamics, order, and molecular conformation of micellar zwitterionic (Decyldimethylammonio)propanesulfonate."
Journal of Physical Chemistry, 1987, 91, 5279

II. **Mikael Jansson, Per Linse and Roger Rymdén.** "Evaluation of micellar radii and counterion binding from self-diffusion coefficients as applied to ionic/zwitterionic mixed micellar systems."
Journal of Physical Chemistry, Submitted

III. **Mikael Jansson and Roger Rymdén.** "Counterion binding in aqueous solutions of mixed micellar aggregates from self-diffusion measurements."
Journal of Colloid and Interface Science, 1987, 119, 185

IV. **Roger Rymden, Mikael Jansson, Katarina Edwards, Mats Almgren and Wyn Brown.** "An experimental study of ionic interactions in solutions of mixed lecithin/dicetylphosphate vesicles."
Journal of Colloid and Interface Science, Accepted

V. **Mikael Jansson and Peter Stilbs.** "A comparative study of organic counterion binding to micelles with the Fourier transform NMR self-diffusion technique."
Journal of Physical Chemistry, 1985, 89, 4868

VI. **Mikael Jansson and Peter Stilbs.** "Organic counterion binding to micelles. Effects of counterion structure on micellar aggregation and counterion binding and location."
Journal of Physical Chemistry, 1987, 91, 113

VII. **Mikael Jansson and Bengt Jönsson.** "Influences of counterion hydrophobicity on the formation of ionic micelles.
Journal of Physical Chemistry, Submitted.

VIII. **Bengt Jönsson and Mikael Jansson.** "Self-diffusion in colloidal systems".
Preliminary manuscript

IX. **Mikael Jansson, Puyong Li, Ulf Henriksson and Peter Stilbs.**
"Orientation and dynamics of a micellarly associated organic counterion".
Journal of Physical Chemistry, Submitted.

1 INTRODUCTION

Surfactants are amphiphilic molecules containing both a hydrophilic, water-attracting, part and a hydrophobic, water-repelling, part. The hydrophilic part can be an ionic, a zwitterionic or a dipolar group, whereas the hydrophobic part usually consists of one or two hydrocarbon chains. At sufficiently high concentrations, surfactants assemble at interfaces or form aggregates in aqueous solutions in such a way that while the hydrophilic parts maintain their hydration the hydrophobic parts are no longer in contact with water. In dilute aqueous solutions of amphiphiles, the aggregates formed are generally micelles or vesicles. However, depending on concentration and temperature, there is a whole hierarchy of other structures which can be formed (1).

Micelles and vesicles may be used as model systems for investigations of the more complex biological membranes. The main components in the membrane are the amphiphilic lipids, which by spontaneous association form a matrix where proteins, enzymes, carbohydrates and stereols can function. Many processes in biological membranes, e.g. permeation, fusion, and structural transformation depend critically on electrostatic forces and ion interactions. Physico-chemical studies of the charged interface and its interactions with ions, which this thesis is partly focused on, are conveniently carried out in model systems.

In the present study vesicles and micelles formed by mixtures of amphiphiles are examined. By changing the composition of the mixed aggregate, fundamental properties of the micelle, such as the surface charge density and the intra-aggregate interactions, are altered. The relation and interplay between different characteristics of the surfactant aggregate, i.e between ion binding and surface charge density, or between surfactant headgroup interaction and molecular conformation, may in this way be examined. In Papers I-III this is applied to mixed micellar systems, whereas Paper IV concerns mixed surfactant vesicles. Papers V-IX deal with micelles formed by surfactants with organic hydrophobic counterions. Due to

the amphiphilic nature of these counterions, a large fraction of ions is micellized, i.e the hydrocarbon part of the counterion is in contact with the hydrocarbon moity of the micelle. Hence, micelles formed by these surfactants may also be regarded as mixed micelles.

2 SURFACTANT SYSTEMS

Surfactants may be classified on the basis of their polar headgroups, which are cationic, anionic, nonionic or zwitterionic. In Table 1, which contains the surfactants used in this work, examples of all categories are found.

Table 1

Anionic	**Cationic**
Lithium dodecyl sulfate (LiDS)	Decylammonium acetate (DAAc)
Cesium dicetyl phospate (DCP)	Dodecylammonium acetate (DDAAc)
Zwitterionic	
Phosphatidylcholine (PC)	
Decyl dimethyl-3-ammonio-1-propanesulfonate (DAPS)	
Dodecyl dimethyl-3-ammonio-1-propanesulfonate (DDAPS)	
Nonionic	
Tetraethylene glycol dodecyl ether ($C_{12}E_4$)	
Hexaethylene glycol dodecyl ether ($C_{12}E_6$)	
Octaethylene glycol dodecyl ether ($C_{12}E_8$)	

Table 1. The investigated surfactants and the abbreviations used in the summary.

The formation of small isolated surfactant aggregates in water is due to the balance between two opposing forces; the hydrophobic effect and the surfactant headgroup interactions. The hydrophobic effect denotes the unfavourable free energy term associated with the contact between water and hydrocarbon. Aggregation is counteracted by the repulsion between charged or dipolar hydrophilic headgroups on the aggregate surface. A compromise is reached by the formation of small aggregates with high surface curvature, where these repulsions are smaller than in the larger macroscopic aggregates with the lower surface curvatures.

At low concentrations surfactants normally aggregate to form micelles. The concentration at which micellization occurs is known as the critical micelle concentration, generally abbreviated as the cmc. The concept of a critical concentration for the formation of micelles from free amphiphiles is inexact but convenient. However, the transition from the unassociated amphiphile state to the micellar state does in fact occur over a narrow critical range of concentration, approaching a phase separation in sharpness (3). Table 2 contains some of the surfactant cmc values used in the thesis.

Table 2

Surfactant	CMC (mM)
PC	$\sim 10^{-6}$
$C_{12}E_6$	0.08
$C_{12}E_8$	0.98
DDAPS	3
LiDS	9
DDAAc	13
DAPS	36
DAAc	61

Table 2. Cmc values of some of the investigated surfactants.

The size of the hydrophobic part plus the nature of the amphiphile headgroups and counterions are factors of importance for the cmc. The latter, i.e. the influence of counterions on cmc, have been investigated both experimentally and theoretically in Papers V-VII.

As mentioned above, amphiphilic molecules associate into a variety of structures in aqueous solutions. Theoretical models of association behaviour of amphiphiles have today reached a level where they can be used in a predictive fashion. An example is the powerful thermodynamic model proposed by Jönsson and Wennerström, from which complete phase-diagrams of multicomponent systems can be calculated (4). In order to understand these

structural aspects one requires an understanding of how the interaction between amphiphiles within aggregates are affected by solution conditions. Qualitatively, this can be rationalized by introducing the dimensionless packing ratio $v/a_o l_c$ (1), where v is the volume of the hydrocarbon chain, a_o the surface area of the headgroup, and l_o the length (~90%) of the extended amphiphile alkyl chain length. It has been shown that different values of the packing ratio correspond to different favoured aggregate geometries. A more general use of the packing parameter is to relate it to the curvature of surfactant aggregates. An increase in the packing parameter is correlated to a decrease in the curvature of the aggregate and, hence, an increase in the aggregate size. Since the effective headgroup area of surfactants is correlated to the repulsive interactions between the ionic or dipolar headgroups, changes in these interactions, such as a more effective screening of the coulumbic interactions, will cause changes in micelle size and shape. In mixed micelles the intramolecular headgroup repulsion depends strongly on the surfactant composition. The packing parameter may therefore be used to rationalize the dependence of micellar size with composition. Examples of this are given in Papers II and III.

The mitigation of surfactant head-group repulsions by counterions is an important aspect of micelle or vesicle formation of ionic surfactants. It is commonly stated that 50-80% of the counterions are "bound" to aggregates formed by ionic amphiphiles (3). However, the estimated degree of counterion binding varies widely depending on the experimental techniques employed, implying that it is not a well-defined quantity. Since the distribution of counterions is rather described in terms of a continuous distribution function, the concept of a two-site model of bound and unbound ions is clearly a simplification.

The Poisson-Boltzmann equation has been widely used to describe polyelectrolyte systems (5). This equation calculates the electrostatic potential of mean force, which directly provides the distribution of mobile ions. The concentration of the polyelectrolyte may be taken into account through the cell model (6). Although there are several approximations inherent in the Poisson-Boltzmann equation, such as the mean field

approximation and the neglection of ion-ion correlations, the theory gives relevant results. The dependence of counterion binding on micellar surface charge density, size and geometry are, in the general features, reproduced by the theory. In Papers II and IV counterion distributions and degree of counterion binding were calculated by solving the Poisson-Boltzmann equation for different surfactant compositions of mixed micelles and mixed vesicles, respectively.

If counterion-micelle interactions of non-electrostatic origin, such as hydrophobic interactions, is taken into account, the theory has to be extended. This is examplified in Paper VII.

3 EXPERIMENTAL METHODS

This section describes the two major experimental methods used in the study of mixed surfactant systems, NMR self-diffusion and relaxation rate measurements. The first applications of NMR to surfactant of solutions appeared some twenty years ago in the literature. With the recent advent of Fourier-transform techniques as well as high-field superconducting magnetic systems, NMR studies have become highly appropriate for a wide range of problems concerning surfactant solutions (7). Size and structure of aggregates, reorientation and segmental motions of molecules, hydration of polar heads, and counterion binding are topics which favourably can be studied with NMR.

3.1 Self-diffusion measurements

Self-diffusion measurements provide data on molecular organization and phase structure of surfactant systems. Structural changes as well as binding and association phenomena are also conveniently monitored by this method. Self-diffusion measurements using NMR are based on the fact that in a spin-echo experiment incomplete refocusing due to irreversible dephasing of the nuclear spins will result from both intrinsic T_2 relaxation and diffusion of the spins in the slightly inhomogeneous magnetic field, which causes an additional spread in Larmor frequencies. The intensity of the spin-echo will thus depend on both T_2 relaxation and diffusion of the molecules, in which the nuclear spins are situated. This can be utilized by applying a linear magnetic field gradient over the sample, to provide a relation between particle position and NMR frequency. The magnetic field gradient spin-echo technique monitors the net displacement of a molecule in the direction of an applied magnetic field gradient. Self-diffusion coefficients were measured with the Pulsed Field Gradient Spin-Echo (PGSE) technique (8), which consists of a normal Hahn spin-echo sequence and two identical field-gradient pulses. The spin-echo attenuation is given by the expression

$$A(\delta)=F\ EXP(-2\tau/T_2- D(\gamma G\delta)^2(\Delta-\delta/3))$$

where $F(\tau)$ is a factor relating to the J-modulation effects (leading to positive or negative peaks), γ the gyromagnetic ratio of protons, G the magnetic field gradient, T_2 the transverse relaxation time, δ the field gradient duration, Δ the time interval between the gradient pulse, and D the self-diffusion coefficient. For a complete methodological discussion of the PGSE technique the reader is referred to an extensive review on the subject (8). An example of the NMR spectra obtained from a self-diffusion experiment, taken from Paper V, is shown in Figure 3.1.

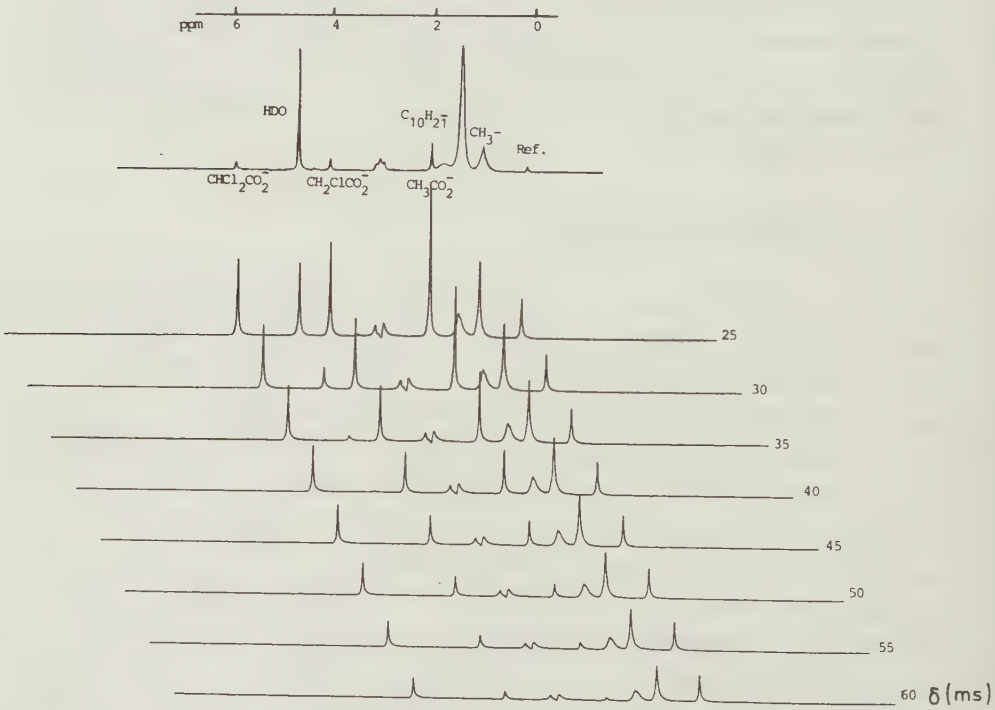

Figure 3.1. An example of a competitive multicomponent self-diffusion FT-PGSE experiment on a mixture of decylammonium acetate, chloroacetate, and dichloroacetate. Above is the normal ^1H NMR spectra, and below a series of spin-echo spectra, where the rate of the decrease of the peak magnitudes with increasing duration of the gradient pulse directly reflects the respective molecular self-diffusion rates.

Self-diffusion coefficients were mainly used to estimate degrees of counterion and amphiphile association to micelles (Paper II-III and V-VI). If a molecule is involved in a exchange between different sites, and the exchange rate is fast with respect to the time-scale of the experimental method, typically in the order of 100 ms, the observed self-diffusion coefficients are population-weighted time averages of intrinsic self-diffusion coefficients in different molecular environments. In the present context, the intrinsic diffusion coefficients are those of molecules (amphiphiles or counterions) in the free or micellar associated state. The effective translational mobility of an amphiphile or a counterion is considerably reduced when it is diffusing with the micelle, and the association process is reflected in a sensitive manner in its time-averaged self-diffusion coefficient. A two-site model has been used to quantify the degree of micellar association of molecules (9);

$$D_{eff} = pD_{mic} + (1-p)D_0$$

where D_{eff} represents the time-averaged diffusion coefficient, p the fraction of micelle associated molecules, D_{mic} the diffusion coefficient of the micelle, and D_0 the diffusion coefficient of the "free" species in the water part (which is measured on a sample with a concentration below cmc). From this simple model one can calculate the fraction of micellarly associated amphiphiles, p_a, and counterions, p_c, respectively. The degree of counterion association, β, is defined as p_c/p_a.

The two-site model is clearly a simplification; the continuous distribution of counterions in the vicinity of a charged micellar surface, and the contribution of intra-aggregate diffusion to the effective self-diffusion coefficient are not represented by the model. This is discussed in detail in Paper VIII, where a theoretical model for calculations of self-diffusion coefficients is presented. However, the two-site model works as a first approximation and has successfully described various association phenomena in a self-consistent way (see e.g. references 10,11).

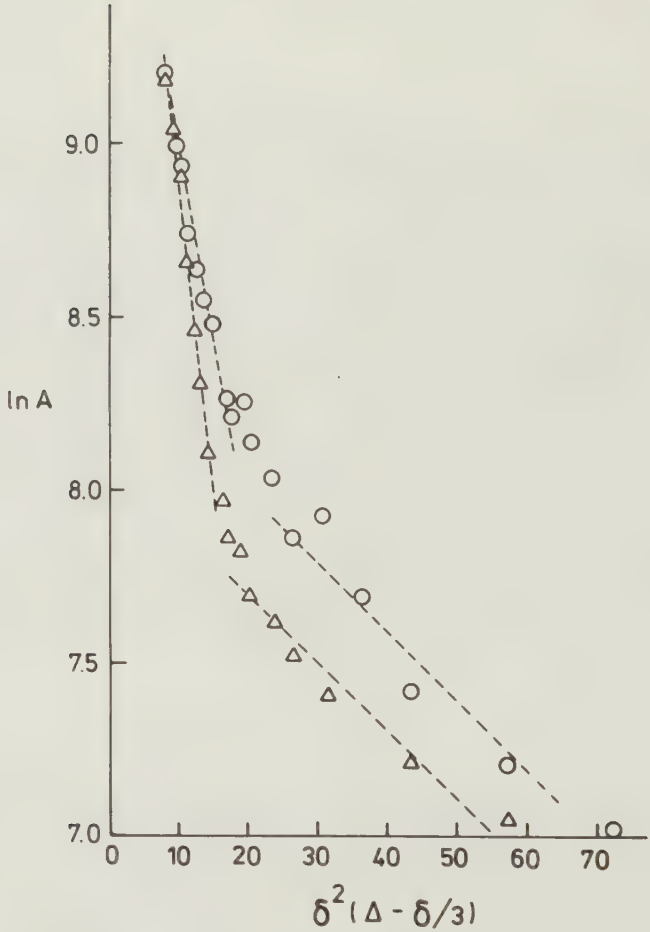

Figure 3.2. The logarithm of the spin-echo amplitude of Li^+ versus $\delta^2(\Delta-\delta/3)$, where δ is the magnetic pulse gradient duration and Δ the interval between the gradient pulses. The systems consist of 1:1 mixed DCP/PC vesicles (the total lipid concentration is 15 mM), where (o)= no divalent ion added, and (Δ)= 0.80 mM Ca^{2+} added.

If the exchange between two different environments of a species is slower than 100 ms, the decay of the spin-echo attenuation will be multi-exponential. This phenomenon is examplified in Paper IV where the self-diffusion of membrane separated populations of counterions were monitored. Deviations from linearity in the plot, shown in Figure 3.2, indicate the presence of restricted diffusion of counterions, originating

from the fraction of counterions inside the vesicle. Qualitatively this reflects that the net displacement, $\langle x \rangle$, becomes less than that of Gaussian diffusion, $\langle x \rangle = 2Dt$, with the membrane barriers present during the time of observation,

Studies of micellar translational diffusion also constitutes a main source of information on the size and shape of micellar aggregates. Micellar self-diffusion coefficients can be measured by monitoring the diffusion of a hydrophobic probe molecule with a negligible solubility in water. Interpretations of D_{mic} in terms of aggregate size are complicated due to the contributions from intermicellar interactions to D. Paper II deals with this problem as applied to mixed ionic/zwitterionic micelles.

3.2 Relaxation rate measurements

Nuclear magnetic spin relaxation is a powerful tool for studying the dynamic nature of surfactant organization and averaged structural properties of surfactant systems. In papers I and IX NMR ^{13}C and ^{2}H spin-lattice relaxation times and ^{13}C nuclear Overhauser enhancements have been used to study the organization and dynamics of both counterions and amphiphiles in micelles. This information have been evaluated by applying the so called two-step model, developed by Wennerström et.al., to the relaxation data (12). This section gives a short description of the theoretical foundations of this model.

In the so-called Redfield limit, i.e, when the motions causing the relaxation are more rapid than the strength of the interaction being averaged, the relaxation rates can be formulated as a product of an interaction constant squared and a linear combination of spectral densites (13). The relaxation equations for isotropic systems are given below. For the deuterium nuclei the spin-lattice relaxation rate is given by:

$$R_1 = (3\pi^2/20)\ \chi^2\ (J(\omega)+4J(2\omega))$$

where χ is the quadrupolar coupling constant. The spin-lattice relaxation

rate and nuclear Overhauser enhancements of a ^{13}C nucleus dominantly governed by dipole-dipole interactions are given by:

$$R_{1i}=(N_i/20)\ (\mu_0\gamma_H\ \gamma_C\hbar/4\pi r^3_{C-H})^2\ (J(\omega_H-\omega_C)$$
$$+3J(\omega_C)\ +6J(\omega_H+\ \omega_C))$$

$$\eta_i=(1/20)\gamma^3_H\ \gamma_C\ (\mu_0\hbar/4\pi r^3_{C-H})^2\ (N_iT_{1i})\ (6J(\omega_H+\omega_C)$$
$$-J(\omega_H-\omega_C))$$

where the index i refers to the i:th carbon along the alkyl chain, μ_0 represents the permeability of vacuum, γ_H and γ_C the magnetogyric ratios of the proton and the carbon nuclei, N_i the number of directly bonded protons to carbon i, $\hbar$ Planck's constant divided by 2π, r_{C-H} the C-H bond length and ω_H and ω_C denote angular Larmor frequencies of protons and carbons, respectively. The $J(\omega)$'s represent various reduced spectral densities at the indicated angular frequencies.

Since the spectral density is the time dependent part of the transition probability per unit time, as induced by fluctuating random fields, it contains detailed information at the molecular level. Molecular motion is commonly quantified in terms of an auto-correlation function of appropriate kind for the Brownian reorientation processes. The key problem with nuclear spin relaxation data is that one cannot directly determine the auto-correlation function from measured spin relaxation data; spin relaxation rates only provide information on the Fourier transform of the auto-correlation function at a very limited number of frequencies. For this reason one has to invoke a motional model for the reorientation processes to go from observed relaxation rates to parameters of the time-domain auto-correlation function for molecular reorientation. It is assumed in the so-called two-step model as applied to spherical micelles that a fast, slightly anisotropic, local chain motion is superimposed on a slow isotropic overall motion of the micelle. If the auto-correlation functions of the fast and slow motions are single exponentials, the relevant reduced spectral densities will be given by:

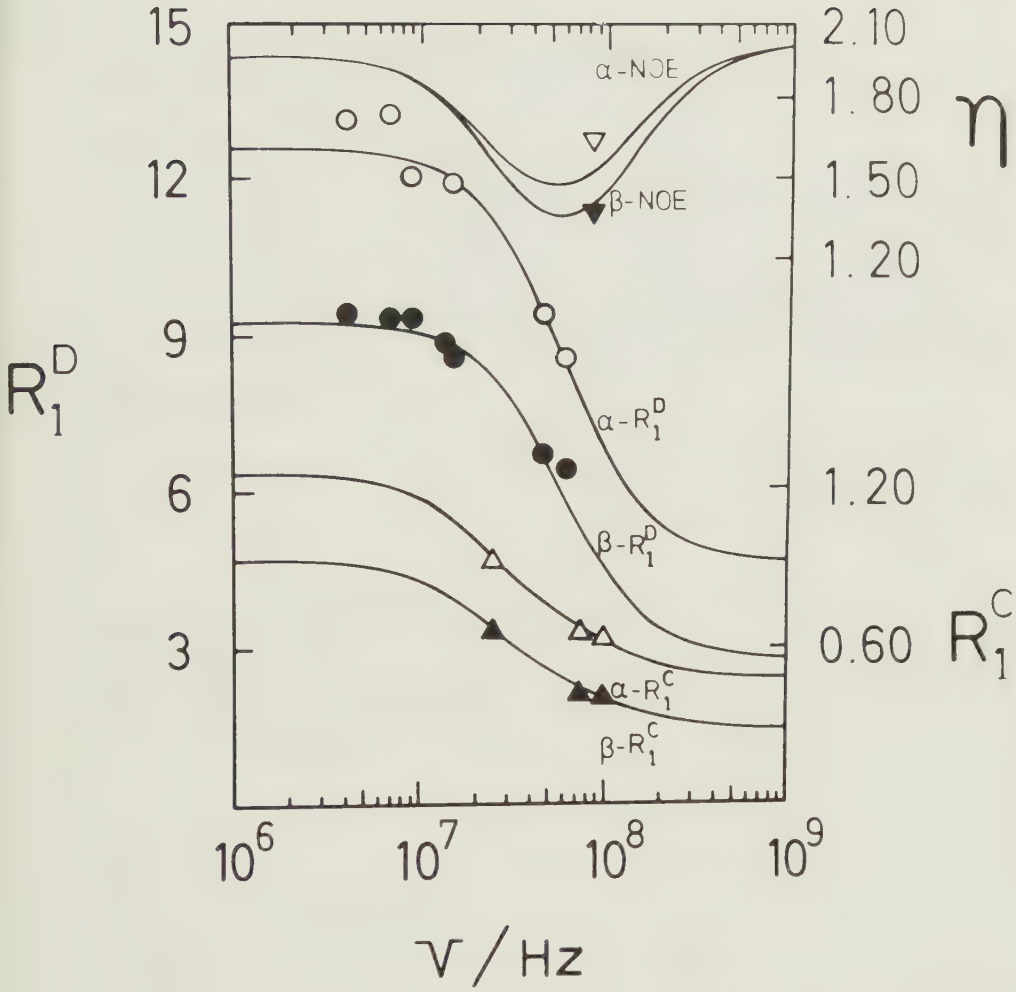

Figure 3.3. Experimental values of R_1^C for the α-carbon (△) and the β-carbon (▲) in butanoate and R_1^D for 2,2-d2 butanoate (○) and 3,3-d2 butanoate (●), respectively. The NOE values of the α-carbon (▽) and the β-carbon (▼) are shown in the top of the figure. The drawn curves correspond to the field-dependence of R_1 and NOE, calculated with the two-step model.

$$J(\omega)=(1-S^2)\ 2\tau_c^{\ f}+2S^2\ \tau_c^{\ s}/(\ 1+(\omega\ \tau_c^{\ s})^{\ 2})$$

$$S=(1/2)\langle 3\cos^2\theta-1\rangle$$

where f and s denote the correlation times of the fast and the slow motions, respectively, S the order parameter and θ the angle between the C-H vector and a local director perpendicular to the micellar surface. The molecular representation of the correlation times would thus be that $\tau_c^{\ f}$ characterizes the local motions of the C-H vector in the alkyl chain, e.g. rotation of the C-H bond due to gauche-trans isomerizations and torsions, whereas $\tau_c^{\ s}$ corresponds to the slower processes of aggregate tumbling and surfactant lateral diffusion at the micelle surface.

An illustration of the experimental and calculated frequency-dependence of ^{13}C and ^{2}H spin-lattice relaxation rates and ^{13}C NOE's is found in Figure 3.3, where the two-step model has been applied to the micellar associated butanoate ion.

In Paper I an attempt was made to extract the spectral densities directly, without invoking any motional model, and thus testing the inherent assumptions of the two-step model. By using Redfield formalism one can reformulate the standard bandshape expressions (14) in terms of individual spectral densities. For a spin ½ (^{13}C) coupled to a spin 1 nucleus, the bandshape is given by (15):

$$I(\omega)=-\mathrm{Re}\{1^t.(A-i\omega I)^{-1}.1\}$$

where $I(\omega)$ is the absorption intensity of the spin ½ (^{13}C) at frequency ω, I a unit matrix of dimension 3, 1^t the unit vector and A the matrix given by

$$A=\mathrm{diag}(iJ_{C-N},0,-iJ_{C-N})-R^0I+(3\pi^2/20)X^2$$

$$X\begin{bmatrix} -J(\omega_N) & -2J(2\omega_N & J(\omega_N) & 2J(2\omega_N) \\ J(\omega_N) & & -2J(\omega_N) & J(\omega_N) \\ 2J(2\omega_N) & & J(\omega_N) & -J(\omega_N)\ -2J(2\omega_N) \end{bmatrix}$$

where J_{C-N} denotes the scalar coupling constant (rad/sec), ω_N the Larmor frequency of relaxing spin (^{14}N), R^0 a phenomenological transverse relaxation rate for the spin ½ (^{13}C) accounting for all other relaxation contributions and magnetic field inhomogeneities and χ the (^{14}N) quadrupolar coupling constant.

A band-shape analysis was carried out for the resonance peak corresponding to the methyl carbons directly bound to the ^{14}N nucleus in DAPS. The ratio between the spectral densities, $J(\omega)/J(2\omega)$ evaluated from the bandshape analysis and the two-step model were found to be 1.21 ± 0.03 and 1.14 ± 0.11, respectively. Thus, the values agree within experimental uncertainty, providing independent support for the relevance of the two-step model.

4 MIXED MICELLES

This section contains a summary of Papers I-III, which concern mixed micelles. The aim of these papers was to investigate the dependence of counterion binding, aggregate size and molecular conformation on the composition of mixed micelles. All three papers have in common the use of alkyldimethylammonio propanesulfonate surfactants (DAPS or DDAPS) as one of the micellar components. In Paper I the dynamics, order and molecular conformation of micelle associated DAPS in pure and octanol-swollen micelles are examined, whereas paper II and III focuses on the interpretation of counterion and micellar self-diffusion coefficients in mixed micellar systems of DDAPS and ionic surfactants. Paper III, however, deals primarily with mixed nonionic/ionic micelles.

4.1 DDAPS/Alcohol micelles

In paper I the two-step model was applied to multifield ^{13}C relaxation and NOE data to determine order parameters and correlation times of the zwitterionic surfactant DAPS in pure and octanol-swollen micelles. Additional conformational information was obtained from ^{13}C shift measurements, providing semiquantitative data on gauche and trans conformational populations in the alkyl chain (16,17).

Figures 4.1 and 4.2 show the order parameter and correlation time profiles, obtained from the application of the two-step model to field-dependent relaxation rate and NOE data, for a 10 w% solution of DAPS. Both order parameters and fast correlation times decrease from the nitrogen atom towards both ends of the surfactant chain. The high S and τ_c^f values of the nitrogen-bound methylene carbons indicate that the number of possible orientations of the C-H bond are more limited, and that the motion of the alkyl chain is more restricted closer to the charged nitrogen atom. A comparison of the S and τ_c^f profiles with those obtained for ionic micelles (18,19) indicates that the zwitterionic headgroup of DAPS is more firmly anchored at the micellar surface as compared to headgroups of ionic surfactants.

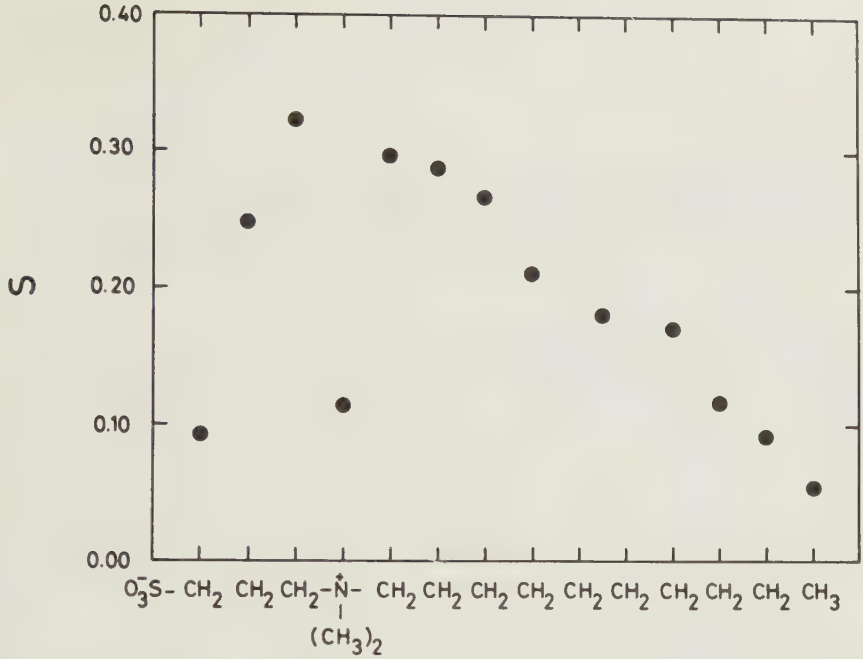

Figure 4.1. The order parameter, obtained from the two-step model analysis of ^{13}C relaxation and NOE data, of 0.36M DAPS at 25 °C as a function of carbon position in the surfactant chain.

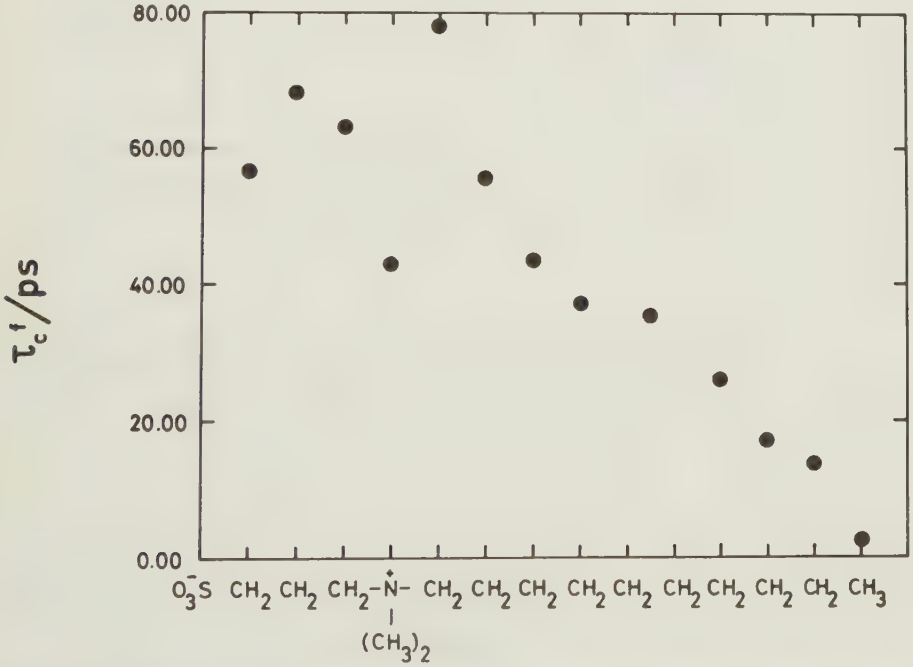

Figure 4.2. The fast correlation time, obtained from the two-step model analysis of ^{13}C relaxation and NOE data, of 0.36M DAPS at 25 °C as a function of carbon position in the surfactant chain.

Conformational information of the micellized DAPS molecules was also obtained from ^{13}C shift data, where the difference in ^{13}C chemical shifts between micellized and nonmicellized DAPS was measured as a function of carbon chain position. In contrast to the other carbons, the nitrogen-bound methylene carbons showed upfield shifts upon micellization of the surfactant. If the upfield shift is interpreted in terms of a conformational change, this implies that the micellization of DAPS induces an increased probability of gauche conformations at these carbons, indicating that the headgroup is tilted relative to the normal of the micelle surface. This conformational interpretation is supported by observations made in studies of other zwitterionic surfactant aggregates (20,21).

Addition of octanol to the DAPS solution was found to have dramatic effects on the micellar association of DAPS. The micelle volume was found to increase with a factor 3 while the monomer concentration of DAPS molecules in the solution decreased from 36 mM to 23 mM, upon the addition of octanol to a molar ratio of 0.23. The influence of octanol on the order parameters and fast correlations times was, however, minor. When taking into account the uncertainty in the S and τ_c^f determinations, no significant differences could be detected between DAPS in the pure and the mixed DAPS/octanol micelles. This demonstrates that the local motions and orientations of the C-H vectors are to a large extent related to intramolecular properties of the surfactant, in line with the results of other studies (22).

Although the comparison of order parameter profiles did not reveal any conformational changes in the DAPS molecule when octanol was added, the ^{13}C shift measurements, which are more sensitive in this context, did indicate such effects. In Figure 4.3 the chemical shift differences of micellized DAPS molecules in DAPS/octanol micelles, as refered to pure DAPS micelles, are represented as a function of carbon position in the surfactant chain. The figure shows that the tendency of downfield shifts on the alkyl chain carbons upon micellization is enhanced with the micellar inclusion of octanol. By comparing the data in Figure 4.3 with those obtained for hexanol and decanol instead of octanol, it was demonstrated that the upfield

shift of the terminal methyl carbon is a consequence of the different hydrocarbon chain lengths of DAPS and octanol.

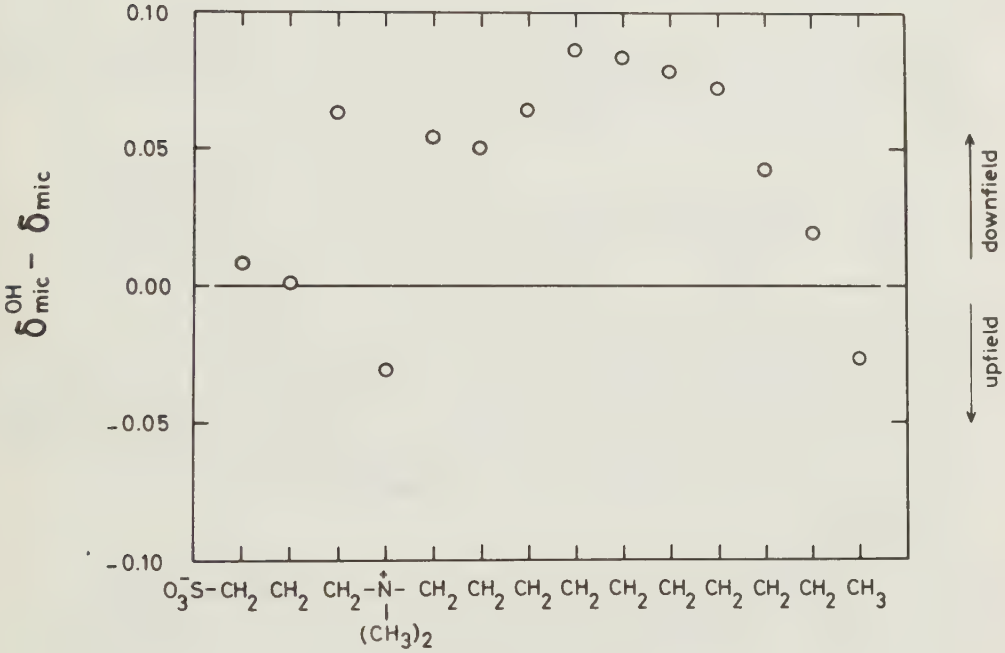

Figure 4.3. The difference in ^{13}C chemical shifts between micellized DAPS in DAPS/octanol micelles and pure DAPS micelles as a function of carbon chain position at 25 ^{o}C.

4.2 Mixed Ionic/Zwitterionic micelles

The systems studied in Paper II regard mixed micelles formed by anionic/zwitterionic and cationic/zwitterionic surfactants. Experimental self-diffusion data of counterions, surfactants and micellar aggregates were obtained for different compositions of DDAPS/LiDS and DDAPS/DDAAc micelles. The radii of mixed micelles were calculated from micellar

self-diffusion data by taking intermicellar interactions into account via a kinetic theory of Brownian motion. Each micellar composition involved a full calculation consisting of four steps calculated iteratively until self-consistency was achieved:

1) A micellar radius was guessed. The micelle was modelled as a charged hard sphere and the effective micelle-micelle potential was assumed to be a simple screened Coulomb potential.

2) The micelle-micelle radial distribution function was calculated from an analytic liquid theory, the Hypernetted Chain approximation (23,24).

3) The potential and the radial distribution function were used to calculate the change in the micellar diffusion coefficient due to micelle-micelle interactions, using the method developed by Ohtsuki (25).

4) A new micellar radius was obtained from the experimental self-diffusion coefficient and the calculated D/D_0 value from the Stoke-Einstein relation.

A general conclusion which can be drawn from the results of the calculations is that electrostatic interactions have to be considered for the interpretation of micellar self-diffusion data, even at low micellar surface charge densities. A substantial reduction in D/D_0, compared to pure DDAPs micelles, was found even at very low contents of ionic surfactant. The calculated radii of the two types of mixed micelles shown in Figure 4.4, reveals a considerably different dependence of mixed micellar radius on composition. The size of the LiDS/DDAPS micelles is larger than the DDAAc/DDAPS micelles over the whole composition range, with a maximum difference in radius at a molar ratio of ionic surfactant of ~0.4.

As a check for consistency, the micellar radii were used as input values in model calculations, based on the Poisson-Boltzmann equation, of fractional ion binding ratios and compared to experimental ion binding data. Figure 4.5 shows that the fraction of bound counterions calculated on the basis of purely electrostatic ion-ion interactions is in remarkably good

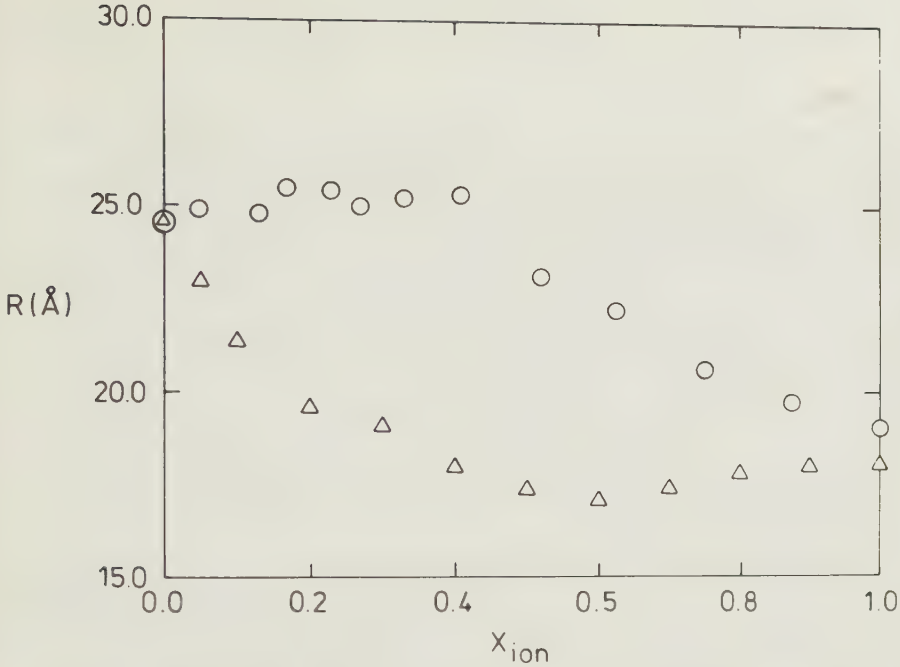

Figure 4.4. Calculated radii of LiDS/DDAPS (○) and DDAAc/DDAPS (△) micelles, versus the molar ratio of ionic amphiphile. The surfactant concentration is 0.1 M at all compositions.

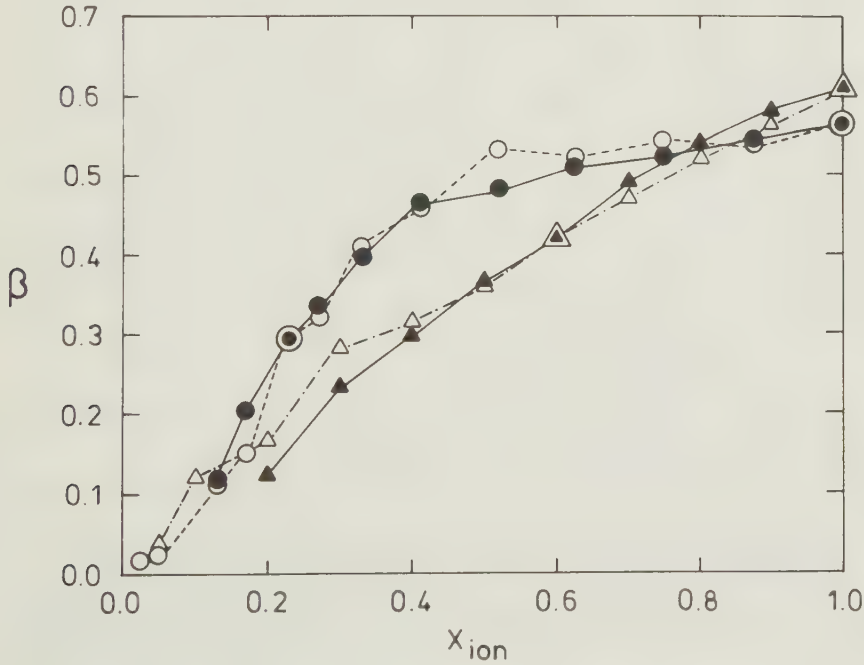

Figure 4.5. Calculated and experimental fractions of associated counterions, β, for the LiDS/DDAPS (● Calc., ○ Exp.) and DDAAc/DDAPS (▲ Calc., △ Exp.) micellar systems, versus the molar ratio of ionic amphiphile.

agreement with the trend of the experimental data for the two systems. This gives support to the present calculation procedure for extracting aggregate radii. Qualitatively, the almost invariant ion binding to LiDS/DDAPS micelles at high molar ratio of LiDS can be understood from the concomitant increase in radius with increasing amounts of added DDAPS. The dilution of the surface charge is thus counteracted by the increase in aggregation number of the mixed micelles. It appears that the ion association of mixed ionic/zwitterionic micelles is dominated by ion-ion interactions and that the influence from ion-dipolar interactions, due to the presence of zwitterionic headgroups, is of minor importance for ion binding.

Although the influence of zwitterionic headgroups on counterion binding seems to be low, they certainly contribute to the headgroup interactions on the micelle surface. Since large effective headgroup areas favour the formation of small micelles, the observation that DDAAc/DDAPS micelles are considerably smaller than those containing LiDS, indicates stronger repulsive surface interactions in the former system. This can be rationalized by assuming that the ionic headgroup interacts more strongly with the positive nitrogen segment of the zwitterion compared to the negativ end. The order parameter and fast correlation time profiles of micellized DAPS molecules, displayed in Figures 4.1 and 4.2, support this conclusion; distinct maxima in S and τ_c^f were found at the nitrogen segment of DAPS, which is consistent with the nitrogen atom being more firmly anchored at the micellar interface than the negativly charged part of the zwitterion. This would indicate a closer packing of headgroups in the case of LiDS/DDAPS due to dominantly attractive ionic-zwitterionic interactions,i.e. a smaller headgroup area as compared to the DDAAc/DDAPS system.

Further evidence for this molecular interpretation of the differences in miceller sizes is given in Figure 4.6. The differences in ^{13}C chemical shifts between carbons in mixed zwitterionic/ionic micelle and pure zwitterionic or ionic micelle are shown in the figure as a function of carbon chain position. The mixed micellar systems are in this case DAPS/sodium decyl sulfate and DAPS/decylammonium acetate, which could be expected to behave similar to the DDAPS/LiDS and DDAPS/DDAAc systems with regard to intermicellar interaction and aggregation. The magnitudes of $\Delta\delta$

of the DAPS carbons are almost 10 times higher than in the DAPS/octanol system (Figure 4.3), which indicates that the chemical shift differences is mainly due to differences in head-group interactions between the mixed and the pure micelles, instead of being caused by pure conformational changes. Since the largest Δδ values of DAPS are found close to the nitrogen segment, and only small differences are detected near the anionic end of the molecule, this indicates that the ionic headgroup interacts more strongly with the positive nitrogen segment of DAPS. Furthermore, a large upfield shift is found for the α-carbon of the anionic surfactant, together with a downfield shift of the same magnitude for carbon-5 of DAPS in the DAPS/anionic system. This is probably a consequence of perturbations of the electron clouds due to the electrostatic attraction between the nitrogen segments of DAPS and the anionic surfactants sulfonate groups.

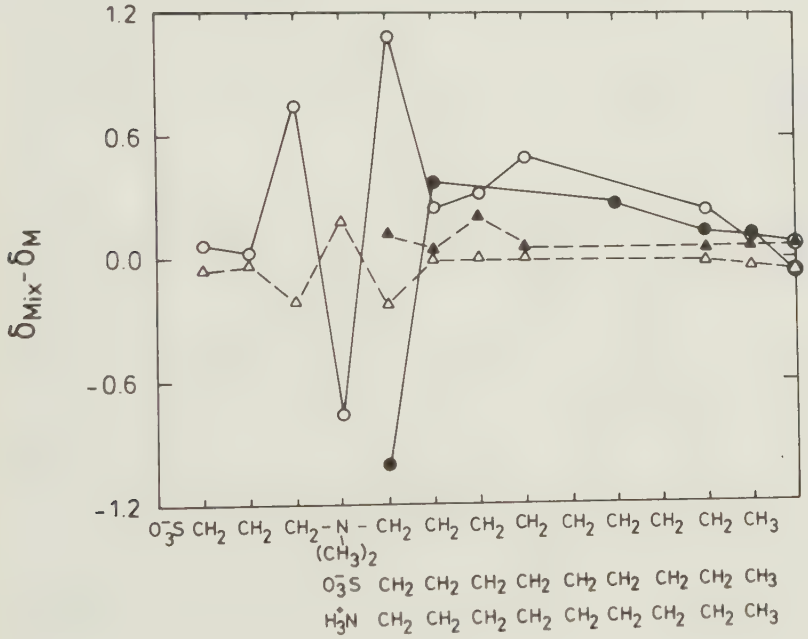

Figure 4.6. The differences in ^{13}C chemical shifts between DAPS in the mixed anionic/DAPS micelle (O), or the mixed cationic/DAPS micelle (△), and the pure DAPS micelle. The differences in chemical shifts between mixed and pure micelles are also shown for the anionic (●) and cationic (▲) surfactants.

It is notable that the trends in $\Delta\delta$ of the DAPS molecules near the micellar surface are mirror images of each other in the two systems. Comparing the trend shown in Figure 4.3 for the DAPS/octanol system with those displayed in Figure 4.6, shows that the DAPS/octanol system in this context resembles an anionic/zwitterionic system.

4.3 Mixed Anionic/Nonionic micelles

The dependence of ion binding on micellar composition was examined in Paper III for anionic/nonionic mixed micelles. The systems studied were mixtures of LiDS and ethylene glycol dodecyl ethers having different ethylene oxide chain lengths ($C_{12}E_n$ n=4,6,8). Mixed LiDS/DDAPS micelles were also included in the study. Surfactant and micellar self-diffusion coefficients were measured in order to estimate changes in micellar size accompanying the variation in the surfactant mixing ratio. However, quantitative calculations of micellar radii from the micellar self-diffusion coefficients, as performed in Paper II, were not carried out.

Figures 4.7 and 4.8 show the degrees of counterion association and the micellar self-diffusion coefficients of the four investigated mixed micellar systems. A large initial reduction in β, as compared to β of pure LiDS micelles, is found at low contents of polyethylene glycol ether surfactants, whereas ion binding is virtually unaffected for the LiDS/DDAPS system. In Paper II is was demonstrated that the invariant ion binding to LiDS/DDAPS micelles with increasing content of DDAPS could be attributed to increasing mixed micellar radii. A comparison of the micellar self-diffusion data of the LiDS/$C_{12}E_n$ and LiDS/DDAAPS mixed micellar systems shows only minor differences in micellar sizes at low nonionic or zwitterionic surfactant concentrations. Hence, the observed difference in the micellar composition dependence of β is probably related to differences in the counterion interaction with $C_{12}E_n$ and DDAPS surfactant headgroups. Kjellander et al. have proposed a model where the polyethylene oxide chains are surrounded by a hydration shell with enhanced structuring

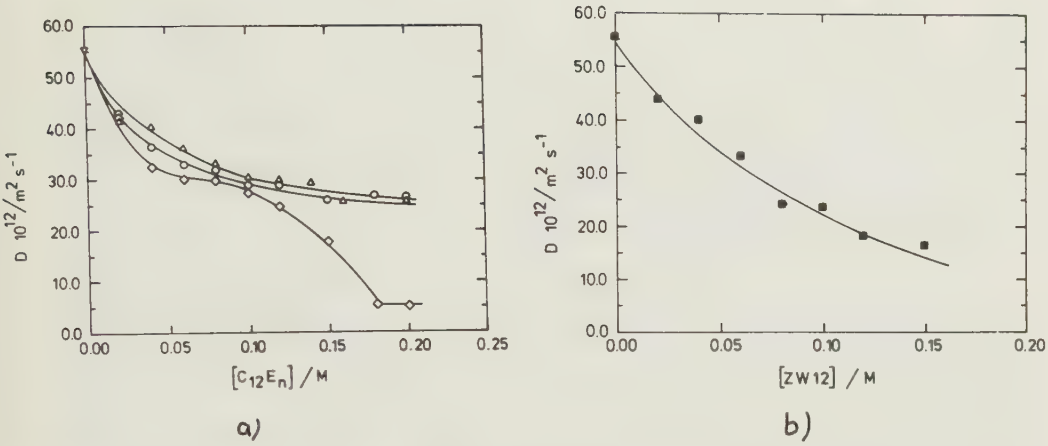

Figure 4.7. a) Experimental micellar self-diffusion coefficients of LiDS/$C_{12}E_4$ (◇), LiDS/$C_{12}E_6$ (○), LiDS/$C_{12}E_8$ (△), and b) LiDS/DDAPS, versus the concentration of nonionic or zwitterionic surfactant. The concentration of LiDS is kept constant at 0.100 M.

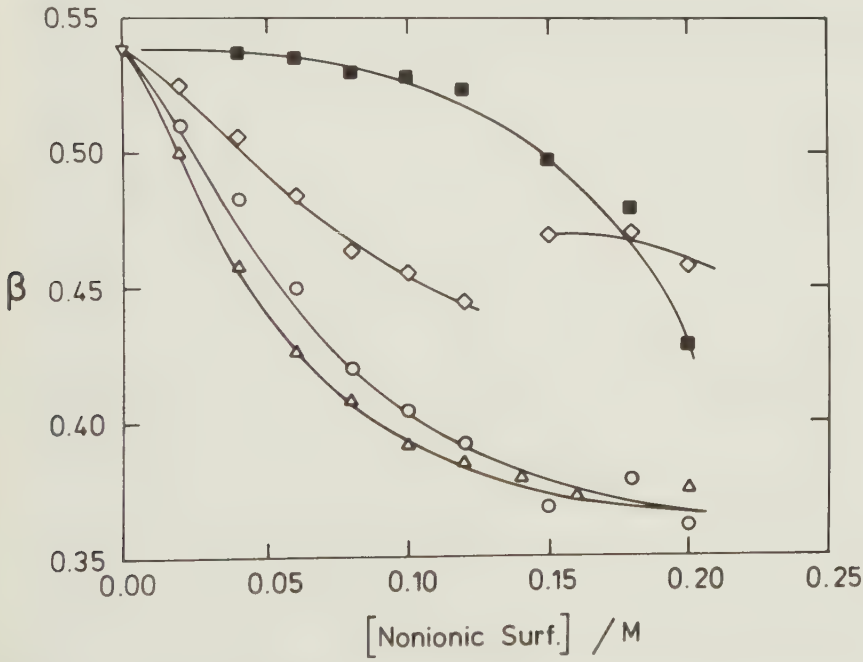

Figure 4.8. β for the micellar systems LiDS/$C_{12}E_4$ (◇), LiDS/$C_{12}E_6$ (○), LiDS/$C_{12}E_8$ (△), and LiDS/DDAPS (■), versus the concentration of nonionic or zwitterionic surfactant. The concentration of LiDS is kept constant at 0.100 M.

of water and a salt-depleated zone, which is attributed to repulsive hydration forces between ions and polyethylene oxide chains (26). This repulsive contribution to the interaction between Li^+ ions and the ethylene oxide groups could explain the lower β values in the LiDS/$C_{12}E_n$ systems compared to the LiDS/DDAPS system.

A correlation between β and aggregate size is found when comparing ion-binding and micellar self-diffusion data in the systems containing $C_{12}E_n$ surfactant, i.e., β decreases and D_{mic} increases in the order LiDS/$C_{12}E_4$, LiDS/$C_{12}E_6$, LiDS/$C_{12}E_8$ at fixed nonionic surfactant concentrations. This may be explained by the influence of the nonionic surfactant headgroup size (repulsive hydration forces) on β, which in turn affects the effective size of the ionic surfactant headgroup (electrostatic screening). This leads to a correlation of low β values to the increased size of both ionic and nonionic headgroups, favouring the formation of small surfactant aggregates.

5 MIXED VESICLES

The interaction of mono- and divalent ions with mixed vesicles formed from an ionic lipid, cesium dicetylphosphate (DCP), and a zwitterionic lipid, phosphatidylcholine (PC), were studied from ^{133}Cs chemical shift measurements in Paper IV. Experimental ion binding data of Cs^+ were compared to a model of ion binding based on the Poisson-Boltzmann equation. The results are shown in Figure 5.1. A good quantitative agreement is observed between experimental and calculated degrees of ion binding at high vesicular surface charge densities, whereas in the low surface charge region the experimental fraction of bound counterions is significantly smaller than predicted by the PB calculations. The observed discrepancy may be an effect of the zwitterionic character of PC, in line with Tanfords discussion of micelles formed by betaines (2). The negative charge of the zwitterions are anchored at the hydrophobic surface whereas the positive charge has considerable motional freedom, and may be taken as part of the diffuse counterion cloud close to the surface. Since the fully charged surface (100% DCP) only binds approximately 65% of the Cs^+ ions, this magnitude of β value gives a sufficient screening of the amphiphile head-group repulsions. Hence, the mobile counterions may avoid the surface at low admixtures of DCP, where the number of "covalently bound" counterions well exceed 65 %.

The system DDAAc/DDAPS, studied in Paper II, is from an electrostatic point of view quite similar to the DCP/PC system, i.e. the counterion has the same charge as the outer end of the zwitterionic headgroup. However, significant differences are found when comparing the DCP/PC ion binding data with the corresponding data for the DDAAc/DDAPS system, displayed in Figure 4.5. Counterion binding is present even at the lowest micellar surface charge densities examined in the latter system. This discrepancy may be a consequence of the two different experimental methods used to quantify counterion binding to surfactant aggregates; counterion chemical shifts for the vesicle system, which samples only counterions in close contact with the aggregate surface, and counterion self-diffusion coefficients in Paper II, which reflect more long-range counterion-aggregate interactions. However, the observed difference may also be related to the specific characters of

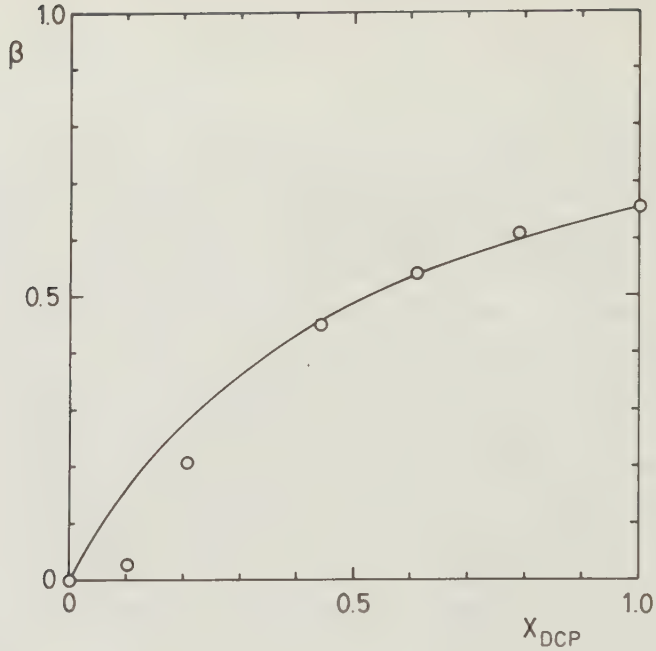

Figure 5.1. The fraction of counterions (Cs^+) bound to DCP/PC vesicles of different composition. The full drawn curve shows the fraction of bound ions obtained from the Poisson-Boltzmann calculations.

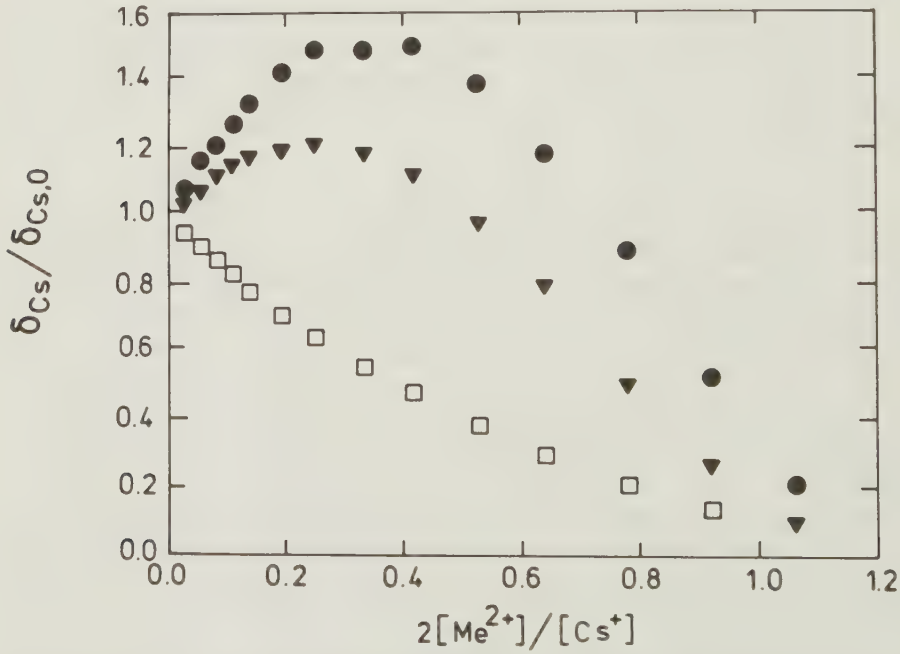

Figure 5.2. The reduced chemical shift of Cs^+ versus equivalent ratio of divalent ions, (□)=Ca^{2+}, (▼)=Co^{2+} and (●)=Mn^{2+} for mixed vesicles with X_{DCP}=0.50.

the molecules and aggregates involved, such as the hydrophobicity of the acetate ion (see section 6.2). Further investigation is therefore needed to clarify this point.

The effect of adding $CaCl_2$ on the binding of Cs^+ to 1:1 mixed DCP/PC vesicles is shown in Figure 5.2. Due to the stronger electrostatic interaction with the membrane, divalent cations are preferentially bound. Consequently, the fraction of bound Cs^+ ions decreases with increasing $CaCl_2$ concentration, which is reflected in a decrease of the reduced chemical shift of Cs^+. Similar measurements were also performed for additions of $MgCl_2$ and $BaCl_2$. The binding of divalent ions was found to decrease in the order $Mg^{2+}>Ca^{2+}>Ba^{2+}$. However, the effects related to ion specificity were found to be rather small. Addition of divalent ions induced, furthermore, a progressive increase in aggregate size, which was monitored by dynamic light-scattering measurements (27). A dramatic increase in the apparent size of the aggregates was observed when divalent ions were added to a point where no Cs^+ ions were bound.

The dependence of the reduced Cs chemical shift on the addition of divalent ions was found to be completly different when substituting Ca^{2+} for the paramagnetic ions Mn^{2+} and Co^{2+}. Figure 5.2 shows that δ/δ_0 increases significantly upon addition of small amounts of $MnCl_2$ and $CoCl_2$. A decrease in the Cs chemical shift is found first at high concentrations of divalent ions. Two competing mechanisms are clearly contributing to the change in δ in this case; δ is shifted downfield by the paramagnetic influence of Mn^{2+} and Co^{2+}, and δ is shifted upfield as the bound Cs^+ ions are expelled from the membrane surface. The observed downfield shift is probably due to the formation of bridged ion-pairs of the type Me^{2+}-DCP-Cs^+ (28,29).

Penetration of the lipid bilayer by divalent ions was indicated from the measurements involving paramagnetic ions. Two clearly distinguishable peaks would have been observed if Mn^{2+} were exclusively located on the outside of the vesicle membrane, which was not the case. Further evidence

for the penetration of the vesicle membrane by divalent ions was obtained from both Li^+ self-diffusion measurements and ^{31}P chemical shift measurements.

6 ORGANIC COUNTERIONS

The vast majority of studies concerning micelles have been performed on surfactants with inorganic counterions. The behaviour of large hydrophobic organic counterions can be expected to be different from that of the smaller and hydrophilic counterions. Due to the pronounced amphiphilic nature of the organic ions, micellization of counterions, as well as amphiphiles, may be expected, leading to the formation of mixed, or catanionic (30), micelles. In Papers V and VI amphiphile aggregation and counterion binding are compared for decylammonium surfactants with different organic counterions, using NMR self-diffusion measurements. Paper VII and VIII focuses on the effects of counterion hydrophobicity on the formation of ionic micelles. Finally, in Paper IX the orientational order and dynamics of a micelle associated organic counterion are investigated.

6.1 Results of self-diffusion measurements

The association behaviour of decylammonium acetate, chloroacetate and dichloroacetate were investigated in Paper V by multicomponent NMR self-diffusion measurements. The cmc's of the surfactants were estimated from the concentration dependence of the diffusion coefficient for the decylammonium ion. Through the application of the two-site model to self-diffusion data of counterions, amphiphiles and micelles, degrees of counterion binding, β, and concentration of amphiphilic monomers in the water part, c^{+}_{free}, were obtained in the concentration range 0-0.25 M.

The invariance of counterion association over a large concentration range, established for several systems (31-33), was also observed here. The β values showed a distinct counterion dependence, ranging from 0.60 for acetate to 0.78 for dichloroacetate, which may be attributed to differences in counterion polarizability. In order to study the competitive effects β was also obtained for surfactant mixtures. As a general net result, the preferential binding of the most associated counterion in the single-ion case was amplified even further. In the 1:1 decylammonium acetate/dichloroacetate system β was found to be 0.44 and 0.92 for acetate and dichloroacetate, respectively.

The cmc's of decylammonium acetate, chlorocetate and dichloroacetate were estimated to be 0.061 M, 0.043 M, and 0.027 M, respectively. Hence, a low cmc is correlated to a high β. Qualitatively, this may be attributed to more effective screening of electrostatic repulsive interaction between decylammonium ions on the micellar surface, when β is high. Differences in concentration dependence and magnitude of c^+_{free} were also observed. The rate of decrease in c^+_{free} was found to be larger in the acetate system than in the other systems. The almost invariant magnitude of β with surfactant concentration, observed for the decylammonium dichloroacetate system, may however be a consequence of errors induced by the application of the two-site model to the diffusion data: Micellar self-diffusion coefficients indicate the formation of elongated aggregates as the surfactant concentration is increased above 0.050 M. Since the contribution from intra-aggregate diffusion to the self-diffusion coefficient of the amphiphile, which can be anticipated to be of importance in micellar systems consisting of larger aggregates, is not taken into account, the calculated c^+_{free} value becomes too high.

The investigation of micelles formed by surfactants with organic counterions was continued in Paper VI, where counterions with more pronounced hydrophobic characters were studied. Figure 6.1 shows β as a function of counterion hydrophobicity (estimated from partition coefficients of the solute between water and octanol (34)). The counterions in the figure are divided into four categories; unbranched (●), branched (▲), monochlorine-containing (○) and dichlorine-containing (◇) counterions. As the increase in β with counterion hydrophobicity is almost identical for the first three categories, the direct dependence of β on counterion hydrophobicity is demonstrated. The branched counterions exhibit generally lower β values than their unbranched counterparts. Similar observations have been made in studies of micelle solubilization of hydrocarbons, where the branched-chain solubilizates were found to have a considerably lower degree of solubilization than their n-alkyl analogues (35).

The distinct correlation between the amount of bound counterions and the aggregation behaviour of the amphiphile is demonstrated in Figure 6.2, where β is shown as a function of the surfactant cmc. As β shows an almost

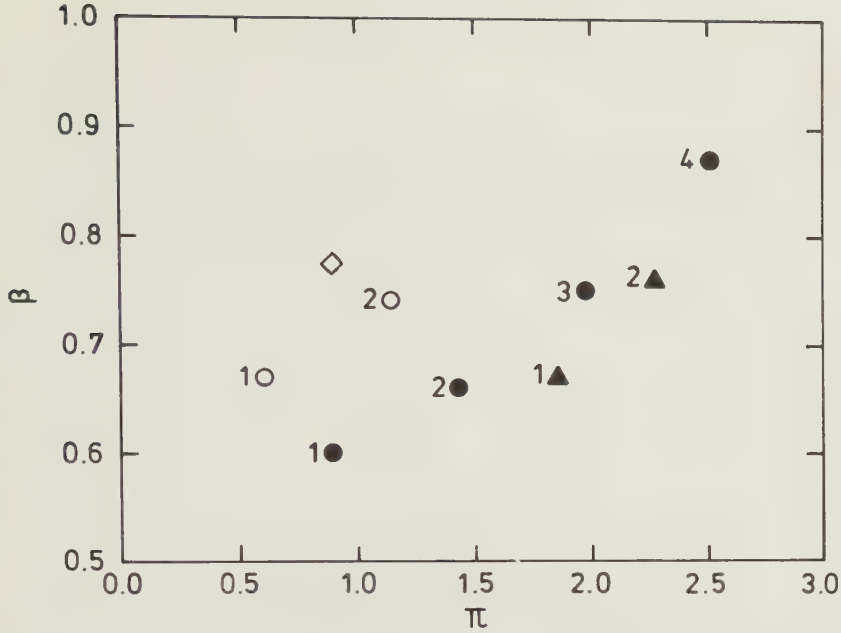

Figure 6.1. β vs. the hydrophobicity parameter, Π. The counterions are indicated by numbers and symbol: 1●,acetate, 2●,propanoate, 3●,butanoate, 4●,pentanoate, 1▲,isobutanoate, 2▲,trimethylacetate, 1○,chloro-acetate, 2○,chloro-propanoate, and◇ dichloroacetate.

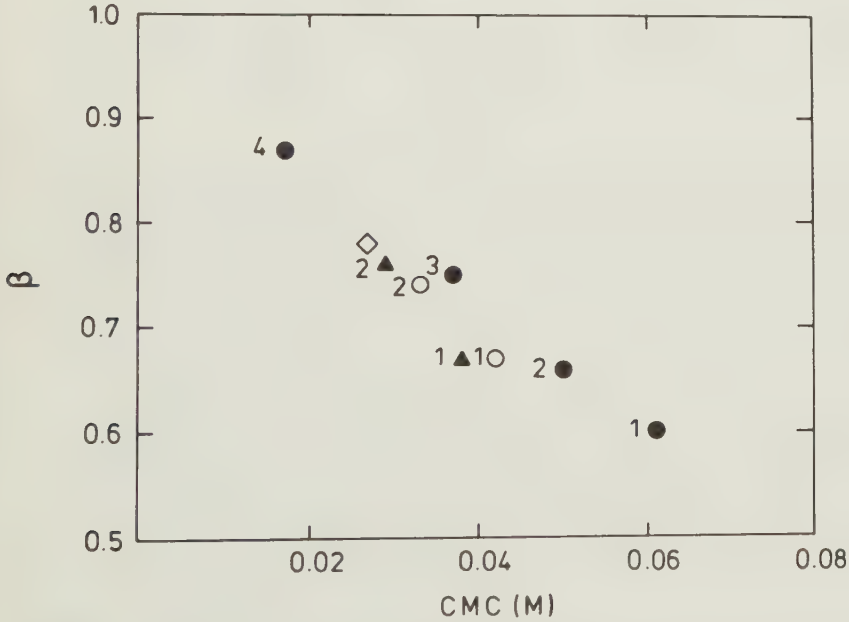

Figure 6.2. β versus cmc. The counterion symbols are the same as above. The cmc's of 1● -4● were determined from density measurements (Paper VII), whereas the others were obtained from self-diffusion measurements.

linear dependence on cmc for all counterions, hydrophobic as well as polarizable, it seems as if the nature of the micelle-counterion interaction is of small significance for the magnitude of the cmc.

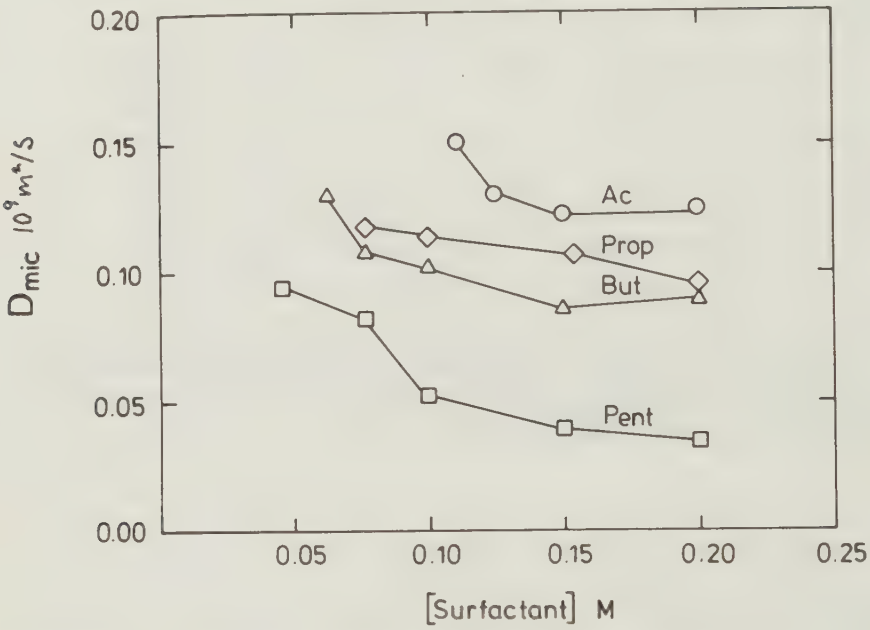

Figure 6.3. The measured micellar self-diffusion coefficients of decylammonium acetate (○), propanoate (◇), butanoate (△) and pentanoate (□) micelles versus surfactant concentration.

Figure 6.3 shows the measured self-diffusion coefficients of some of the investigated decylammonium systems as a function of surfactant concentration. A general decrease in D_{mic} is observed with increasing surfactant concentrations, which can mainly be attributed to increasing micelle-micelle repulsions. This was shown in Paper VIII, where an alternative method of estimating the contribution of intermicellar interactions to D_{mic} to that used in Paper II was presented. This method is based on estimations of the change in the electrostatic free energy of the cell when the cell radius is altered. Figure 6.3 also shows that low D_{mic} values are correlated to large counterion sizes, which

indicates a correlation between the micellar size and β. The dramatic decrease in D_{mic} found for the pentanoate system above 70 mM is due to the formation of larger elongated micelles.

6.2 A Theoretical Model

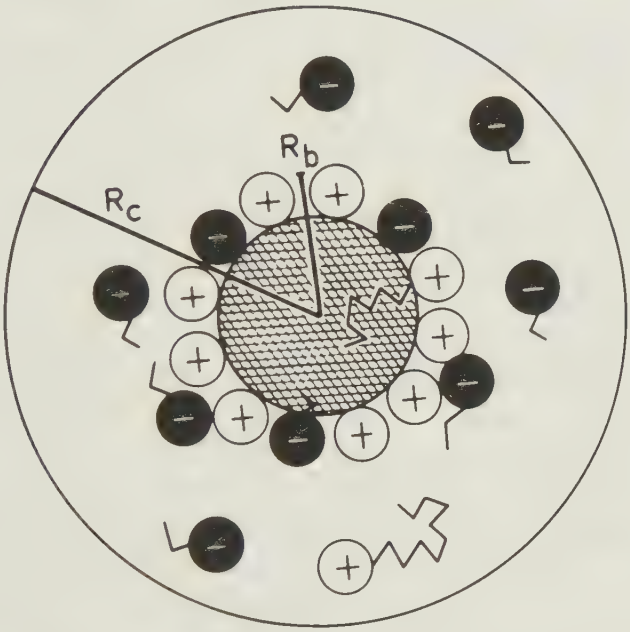

Figure 6.4. A schematic picture of the micellar model used. The system consist of molecules in the micelle and water part. Both decylammonium ions and hydrophobic counterions contribute to the hydrocarbon part of the micelle (for clarity only one hydrocarbon tail of each species is indicated in the micelle). The micellar radius, R_b, and cell radius, R_c, are shown.

The distribution of counterions in the vicinity of charged micelles is usually described by the Poisson-Boltzmann theory. If interactions between counterions and micelles of non-electrostatical origin are also to be considered, the theory clearly has to be extended. In Paper VII a micellar model is proposed which takes into account the hydrophobic interaction

between the micelle and the counterions. In this model the micellization of both amphiphiles and counterions were considered. The distributions of amphiphilic ions and counterions between the micelles and the water part were calculated from the expressions of the chemical potentials of the molecules in the micellized and the water part, together with the condition that the molecules in the two sites are in chemical equilibrium. Free-energy differences between the molecules in the two states stem from differences in electrostatic interactions, mixing entropies and hydrophobic interaction, which have been discussed in detail in reference 36. With the combined use of the expressions for the chemical potentials and the Poisson-Boltzmann equation, the total distribution function of both the amphiphile ions and the counterions in the micellar system, modelled by a cell model, could be obtained.

An important parameter in the model calculations is the difference between the standard chemical potential of counterions in the micelle and the water part, $\Delta\mu_c°$, which may be regarded as the hydrophobic free energy of the counterion. For sufficiently large molecules, it has been shown that the hydrophobic free energy is directly proportional to the size of the hydrocarbon chain (36,37). $\Delta\mu_c°$ was here determined from experimental surfactant cmc's. Figure 6.5 shows that the increment in $\Delta\mu_c°$ per CH_2 group is considerably lower for the smallest counterions than for the more hydrophobic ones. Thus, deviations from the the linear dependence of the hydrophobic free energy on the hydrocarbon size is demonstrated for the smallest molecules.

Although the fraction of micellized counterions obviously depends on the micelle concentration, the molar ratio of counterions in the micelle, as predicted by the model calculations, remains independent of this quantity. X_c was found to increase almost lineary as a function of the counterion size, ranging from X_c=0.30 for acetate to X_c=0.48 for hexanoate. Thus, a substantial amount of acetate ions is micellized, implying that ~60% of the associated ions (as defined by the two-site model) have the methyl group in contact with the micelle hydrocarbon domain. The hydrophobic interaction between the acetate ion and the micelle is, however, rather weak. The calculations show that β for acetate in absence of

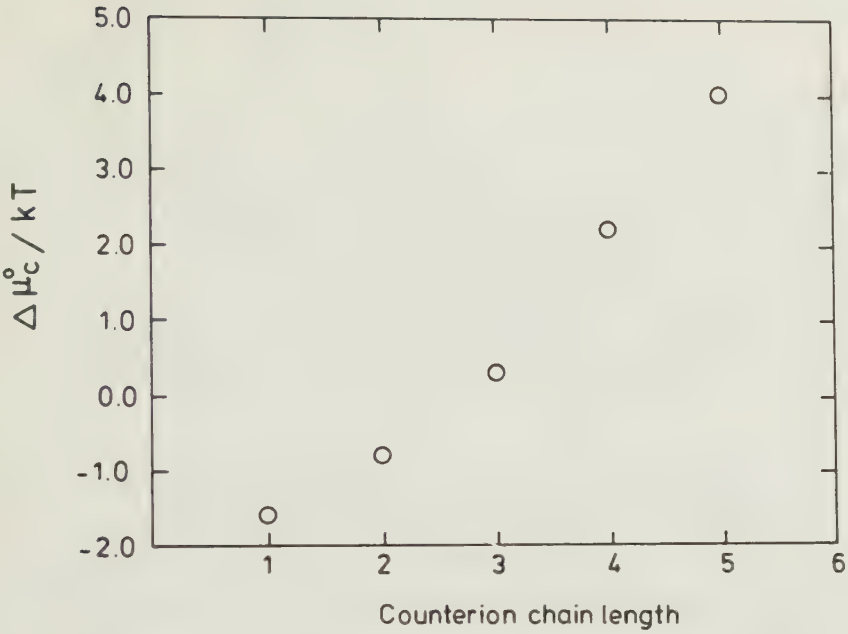

Figure 6.5. The counterion hydrophobic free energy, $\Delta\mu_c{}^\circ$ versus the counterion chain length (the number of methyl or methylene groups in the counterion chain).

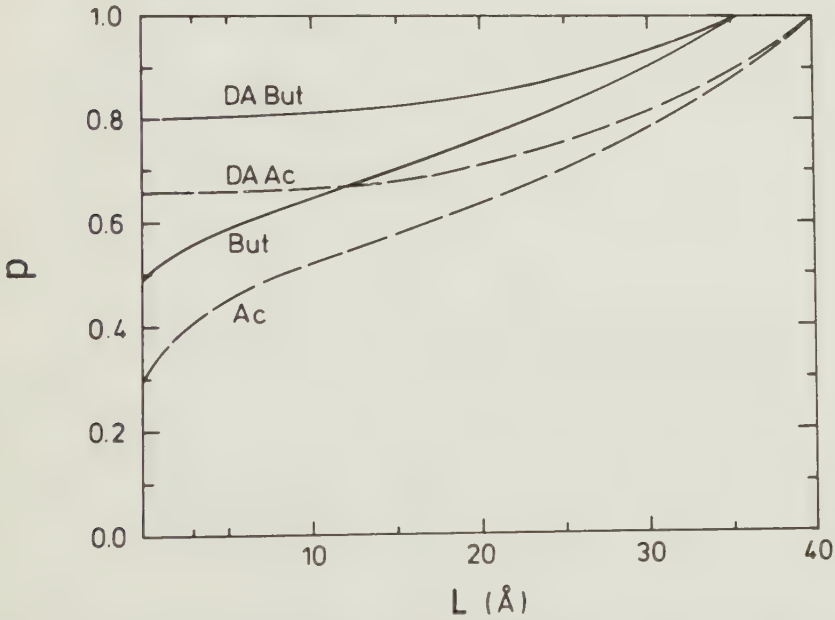

Figure 6.6. The calculated fraction of molecules confined within a distance L from the micelle surface versus L for the decylammonium ion (DABut) and the butanoate ion (But) in the decylammonium butanoate system, and the decylammonium ion (DAAc), and the acetate ion (Ac) in the decylammonium acetate system. The surfactant concentrations are 0.15 M.

hydrophobic interactions is 0.56, as compared to 0.62 when hydrophobic interactions are taken into account. Hence, the high X_c of acetate may be compatible with the qualitative agreement between the the Poisson-Boltzmann theory and the observed β values of acetate ions displayed in Figure 4.5. It is notable that β for acetate ions is 0.06 higher than for lithium ions, i.e. the same difference as predicted by the model.

Due to the large amount of micellized counterions in the systems containing the most hydrophobic counterions, the effective surface charge density of these micelles become very low. Since lower surface charge densities are in general related to the formation of larger aggregates, this explains the formation of the large micelles observed in the decylammonium pentanoate system.

The main output of the model calculations is the distribution functions of the amphiphilic ions and the counterions in the cell. Examples of these are given in Figure 6.6. By defining micellarly "bound" ions as those confined within 3 Å from the micelle surface, qualitative comparisons can be made between calculated and experimental β values. The agreement between the measured and predicted β was found to be good, even though the increase in theoretical β values with counterion chain lengh was slightly less progressive than the measured.

Due to the approximations inherent in the two-site model it is preferable to compare the results of the model calculations directly with the measured self-diffusion coefficients. In reference 38 it was shown that the effective self-diffusion coefficient may be calculated provided that the distribution function of the molecule in the cell is known. The actual calculation procedure for doing this is described in detail in Paper VIII. Figures 6.7 and 6.8 show calculated and experimental self-diffusion coefficients for the decylammonium ion and the counterions as a function of the total surfactant concentration for decylammonium acetate, propanoate, and butanoate, respectively. In general very good agreements are obtained between theoretical and experimental D/D_0 concentration profiles, which indicates the relevance of the model proposed. However, the calculated D/D_0 values of the decylammonium ions were found to be

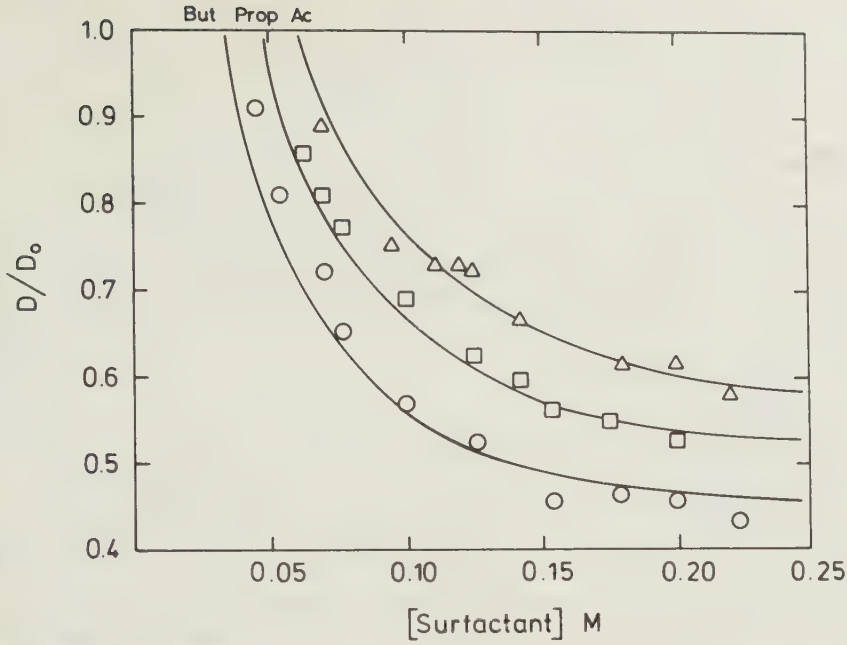

Figure 6.7. The calculated D/D_0 values of acetate, propanoate, and butanoate versus the surfactant concentration. The corresponding experimental D/D_0 values of acetate (△), propanoate (□) and butanoate (○) are also shown.

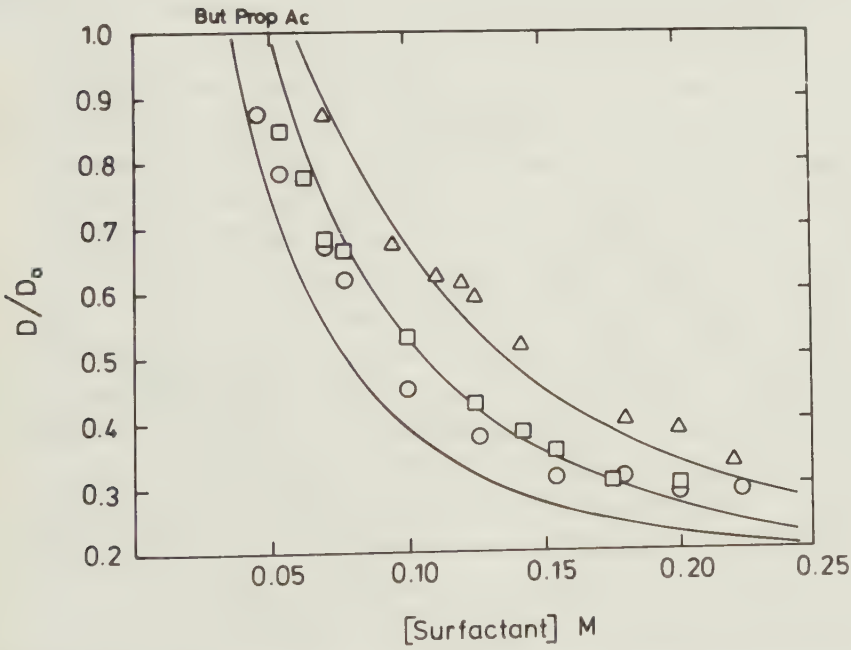

Figure 6.8. The calculated D/D_0 values of the decylammonium ion versus the surfactant concentration. The corresponding experimental D/D_0 values of the decylammonium ion in the decylammonium acetate (△), propanoate (□) and butanoate (○) systems are also shown.

lower than the experimental values in the systems containing the most hydrophobic counterions. This may originate from the formation of elongated aggregates, or the polydispersity of the cell sizes, in these systems,

6.3 Dynamics and orientational order

In Paper VI attempts were made to extract information on the orientation of micellarly bound organic counterions from T_1 excess relaxation rate measurements in the presence of a micelle solubilized paramagnetic relaxation-agent, Tempo. Since the actual location of Tempo in the micelle was not known with certainty, these experiments were not so informative, even though comparisons between the excess relaxation rates of the counterions revealed some interesting differences between the more hydrophobic ions and the other ions. A clearer picture of the orientation of the bound counterion was obtained in Paper IX, where multi-field ^{13}C and ^{2}H relaxation data were collected for 0.2 M solutions of decylammonium butanoate and decylammonium acetate. The data were analyzed within the two-step model for relaxation of micelle associated surfactants. In Figures 6.9 and 6.10 the calculated order parameters and fast correlation times for butanoate and the decylammonium ions are displayed. Although the magnitudes differ, the general features of the order parameter and fast correlation time profiles of the counterion and the amphiphile are quite similar; S and τ_c^f decrease along the carbon chain towards the terminal methyl group. This implies that the number of possible orientations of the C-H,D bond vector are more limited, and that the motion of the alkyl chain is more restricted closer to the charged headgroup. Since the relaxation rates at the α and β positions in butanoate were found to be almost identical in the non-associated counterion case, this is clearly an effect of the micellar association of the counterion. This supports the concept of the hydrocarbon tail of butanoate being oriented into the micellar hydrocarbon moiety, i.e a micellization of the counterions, which agrees with the model proposed above.

The influence of large hydrophobic counterions on the order and dynamics of the decylammonium ion is demonstrated by comparing order parameters and correlation times of the amphiphile in the decylammonium

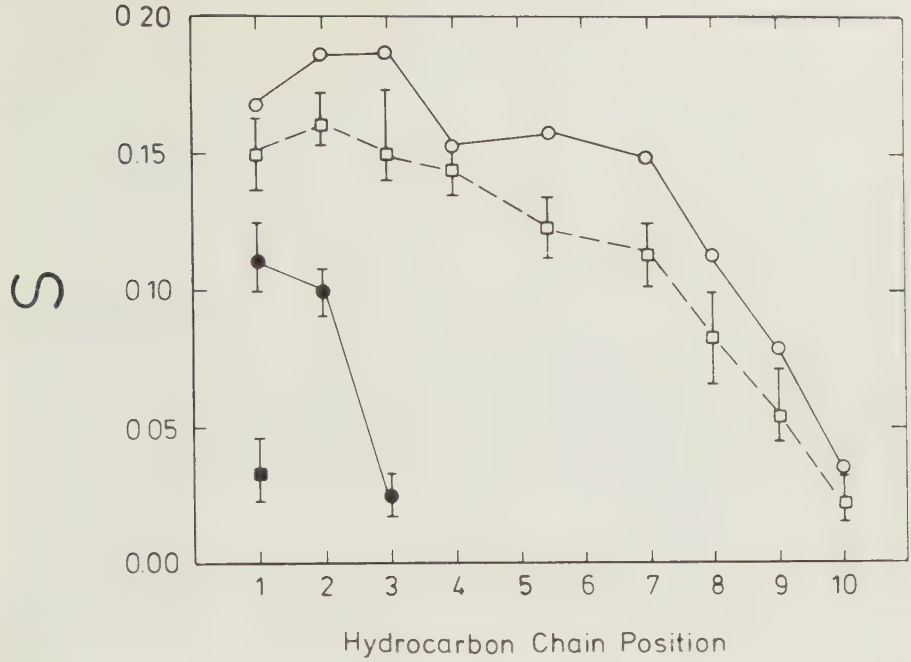

Figure 6.9. Evaluated order parameters versus the hydrocarbon chain position (relative the charge headgroup) for the decylammonium ion in DABut (○), the decylammonium ion in DAAC (□), butanoate (●), and acetate (■).

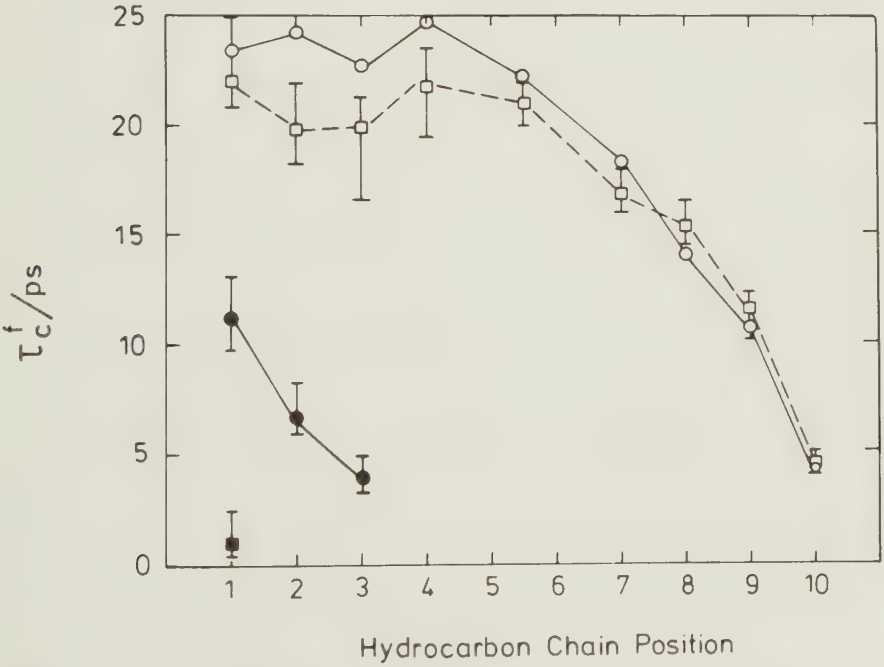

Figure 6.10. Evaluated fast correlation times versus the hydrocarbon chain position (relative the charge headgroup) for the decylammonium ion in DABut (○), the decylammonium ion in DAAC (□), butanoate (●), and acetate (■).

acetate and butanoate systems. Figures 6.9 and 6.10 show that the micellar inclusion of butanoate affects both the order and correlation time profiles of the amphiphile. It is clearly seen that the presence of butanoate increases the order and decreases the mobility of the decylammonium chain. This may be caused by either a closer packing of the alkyl chains due to the reduced electrostatic repulsion between the ionic headgroups in the decylammonium butanoate system, or it may be a consequence of the different packing of the alkyl chains following the micellar inclusion of the hydrocarbon tail of butanoate.

7 CONCLUSIONS

Ion binding

o The magnitude of β depends on the aggregate size (II), the specific counterion-amphiphile headgroup interactions (III), the counterion polarizability (V), hydrophobicity (VI,VII), and geometry (VI).

o Micellar ion binding affects the cmc of surfactants, the concentration of free monomers above cmc (V), micelle sphere-rod transitions (VI) and the dynamics and orientation of micellized amphiphiles (IX).

o Zwitterion-counterion interactions do not contribute to β (II).

Mixed aggregates

o The size of mixed aggregates depends on changes in amphiphile headgroup repulsions with composition (II,III).

o Headgroup interactions in mixed ionic/zwitterionic aggregates depend critically on the orientation of the zwitterion (II).

o The conformation of amphiphiles in "pure" and mixed aggregates differs slightly (I,II).

o Hydrophobic organic counterions are to a large degree micellized (V-IX).

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